Effect of Reaction Conditions on the Distribution of Hydroxyl Functional Groups in HEA-BMA Copolymer

Loretta Idowu

Abstract
Keywords: copolymer composition distribution; radical polymerization kinetics; semi-batch starved feed; hydroxyl-functionality

Non-functional monomer feedstocks containing alkyl meth(acrylate) components such as butyl acrylate (BA) and butyl methacrylate (BMA) have been replaced or augmented with functional monomers such as 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA) to produce reactive polymer chains, through hydrogen bonding, of lowered molecular weight (MW) for application in solvent-borne automotive coatings. The polar and functional reactants affect the radical copolymerization kinetics and final copolymer composition, and introduce solvent dependencies. A series of BMA/HEA experiments have been performed at 138 °C to determine the influence of these changing kinetic parameters under starved-feed semi-batch operating conditions. A comparison with BMA/BA copolymerization shows that the influence of hydrogen bonding is small, with the semi-batch system well controlled to HEA contents of up to 50 wt%. Aside from controlling the overall copolymer composition, understanding the distribution of the hydroxyl functional groups among the polymer chains is of importance, as non-functionalized lower-MW chains will not crosslink into the polymer network formed upon application of the coating. A series of BMA/HEA copolymers containing 6.25, 12.5 and 25 wt% HEA were synthesized with weight-average polymer MWs varied between 3000-10000 Da through manipulation of reaction temperature and initiator loading (2 to 4 mol% relative to monomer) during starved-feed semi-batch operation.
Synthesis and Utilization of Low Dispersity Acrylic Macromonomer as Dispersant for Non-Aqueous Dispersion Polymerization

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ABSTRACT
Key Words: Atom transfer radical polymerization, cobalt chain transfer polymerization, nucleophilic substitution, non-aqueous dispersion polymerization, macromonomer

Non-aqueous poly(acrylic) dispersions (NADs) used in automotive coating formulations are heterogeneous high-solids suspension of polymeric nano-size particles (< 200 nm) produced by radical polymerization in organic hydrocarbon medium. An important component of the system is the low molecular weight (MW) reactive polymeric dispersant (5000-6000 Da), which stabilizes the particles formed. A vinyl-terminated butyl methacrylate (BMA) macromonomer dispersant synthesized by cobalt chain transfer (CCT) polymerization has been shown to be more effective at stabilizing the nanoparticles formed during the NAD synthesis than a BMA based grafted dispersant with vinyl groups attached at random positions along the backbone. The macromonomer, although having controlled double-bond placement through CCT chemistry, still have a molecular weight dispersity of close to two (Figure 1A). While the role of dispersity of a self-assembling amphiphilic block copolymer has been studied in emulsion polymerization, no such study exists for dispersion polymerization, which commences as a homogeneous solution. Thus, we have synthesized a low dispersity P(BMA) macromonomer (Đ < 1.3, Figure 1B) by sequential application of ATRP and catalytic chain transfer polymerization using bis(difluoroboryldiphenylglyoximato)cobalt(II) [CoPheBF] of similar number-average MW and terminal double bond functionality. Using both methyl acrylate homopolymerization and methyl methacrylate/methyl acrylate (70/30 w/w) copolymerization to produce NADs, the lower dispersity P(BMA) macromonomer provides better stabilization per dispersant chain, as characterized by smaller average particle size and higher weight fraction of incorporated dispersant ($W_{inc}$). These results show directly (to the best of our knowledge, for the first time) the advantage of narrowing the dispersity of reactive dispersant with TDB functionality used to stabilize non-aqueous dispersions.

Figure 1. Two P(BMA) macromonomers tested as reactive dispersants in non-aqueous dispersion
Hydrolytic Degradation of Reactively Modified PLA

Heather Simmons

ABSTRACT
Poly(lactic acid) (PLA) is a bioderived and biodegradable thermoplastic polyester which attracts wide interest as a viable replacement for traditional petroleum-based polymers. Recent work in our group showed that substantial improvements in the melt strength, crystallization properties, and strain hardening characteristics of PLA can be achieved through solvent-free, peroxide-initiated grafting of the trifunctional coagent triallyl trimesate (TAM). Given the improved properties of TAM-modified PLA, it becomes relevant to gain a thorough understanding of the effects of these modifications on its long-term hydrolytic degradation characteristics. Changes in mass loss, molecular weight loss, and thermal properties were monitored in relation to the hydrolytic exposure time. A significant reduction in molecular weight was observed along with a narrowing of the molecular weight distributions over time, resulting from the cleavage of high molecular weight fragments from the polymer chains. The comparison of mass loss and molecular weight loss profiles suggested a bulk mechanism as the predominant erosion phenomenon. In addition, hydrolysis induced crystallinity was observed, showing an enhanced chain mobility at the testing temperature and preferential erosion of amorphous regions. The results showed that reactive modification with TAM does not negatively affect the hydrolysis of PLA, thus making this modification approach highly promising for various commodity applications that require degradable polymers.
**Graphene: Improving the mechanical, thermal and electrical properties of polyamide 6,12**

*Quang Binh Ho*

**ABSTRACT**

It is a common practice to add fillers to polymers to change or improve physical and mechanical properties of the composites. In this project, MesoGraf, a commercial graphene product, was introduced into polyamide 6,12 by melt-compounding at a volume content up to 15.3%. Their flexural moduli, impact strength, electrical conductivity, and thermal conductivity were analysed and compared with those of neat polyamide. We found that the flexural modulus and thermal conductivity of the graphene-polyamide composites increased with the graphene content; at 15.3 % v/v, they are 173% and 1335% higher that those of neat polyamide, respectively. The electrical percolation threshold was attained at 2.0 % v/v, and the maximum conductivity (in the order of 10-2 S/cm) at 4.1 % v/v. The results were also compared with polyamide-graphite composites.
Improved Radical Branching of Polypropylene through Functionalized Nitroxyl Chemistry

Michael McLaren

ABSTRACT
Acrylated TEMPO (AOTEMPO) has been used in conjunction with a peroxide initiator to branch linear polypropylene while minimizing gelation. Existing methods of producing long chain branching in linear polypropylene face limitations in efficacy due to the concurrent radical chain scission reaction. The latter is due to the instability of the tertiary carbon macroradicals produced during the radical grafting of crosslinking agents. Existing techniques (relying predominantly vinyl silanes and triacylates) develop bimodal molecular weight distributions, composed of scission-dominated low MW and branch-rich high MW chains (with the latter potentially forming an insoluble gel). Functionalized nitroxyl chemistry hinders chain scission during the grafting process, ensuring a more even distribution of branching functionality across chains. In the present work, linear PP has been branching using AOTEMPO to produce a branched product exhibiting strain hardening, increased storage modulus at low shear rates, and low gel content.
Polymeric Ionic Liquid Compositions for Extractive Fermentation of n-Butanol from Two-Phase Partitioning Bioreactors

Robert Biro

ABSTRACT
Polymeric ionic liquids (PILs) have the possibility to combine the unique properties of monomeric ionic liquids with the macromolecular architecture of polymers, providing novel properties and powerful functions in a variety of applications. The recovery of target molecules from dilute aqueous solutions is one such application, specifically, as the polymeric absorbent phase limiting end-product inhibition in two-phase partitioning bioreactors producing butanol. Uncross-linked PIL’s bearing n-alkyl aliphatic substituents have proven to be most effective, demonstrating high absorption of n-butanol as reported by partition coefficient and butanol/water selectivity values. This work focuses on further developing the range of substituents of PILs, attempting to increase the thermodynamic affinity for the target molecule and decreasing side-chain crystallinity, by synthesizing novel compositions of matter. The resulting polymers physical and chemical properties, were found to be central to its sorption performance of n-butanol and have further implications in the end-goal use of extractive fermentation in two-phase partitioning bioreactors.